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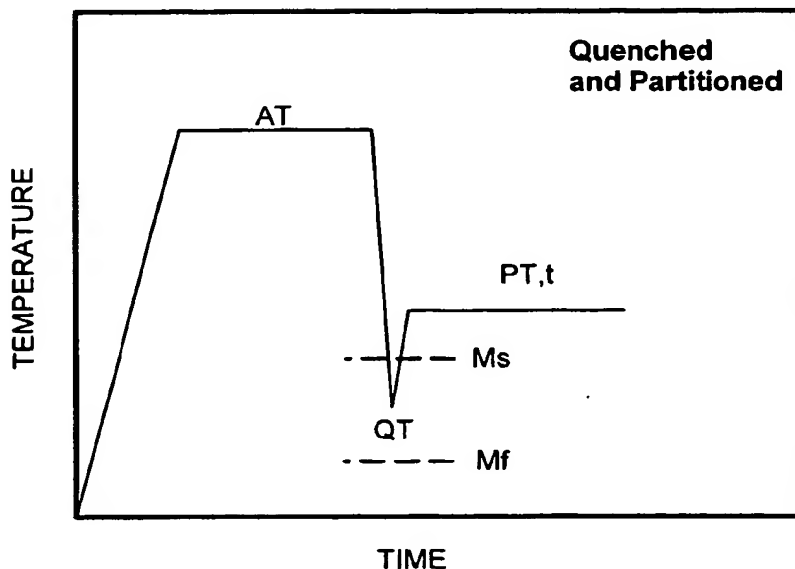
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(54) Title: METHOD FOR PRODUCING STEEL WITH RETAINED AUSTENITE



(57) Abstract: The present invention relates to a process for producing steel with retained austenite. In one embodiment, the process comprises the steps of heating a steel alloy to produce austenite, quenching the steel to produce martensite, and carbon partitioning to transfer carbon from the martensite to the austenite.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR PRODUCING STEEL WITH RETAINED AUSTENITE**FIELD OF THE INVENTION**

The invention is directed to a method for producing steels with microstructures containing retained austenite.

BACKGROUND OF THE INVENTION

The difficulty that this invention seeks to address is that of creating a microstructure in steel, (e.g., but not limited to, low carbon sheet steel) that contains austenite at the ambient temperature at which the steel is to be used in some application, typically room temperature. Without substantial additions of expensive alloying elements such as nickel, austenite usually must be enriched with carbon (or sometimes nitrogen) in order to stabilize it to room temperature. (Actually, it is metastable, and undergoes subsequent transformation to martensite during deformation, a key component of its utility in service.) The problem is to enrich some austenite in the microstructure with carbon, by controlling microstructure evolution and carbon partitioning, without having to use a much higher carbon-containing steel, which is usually undesired for reasons such as reduced weldability.

Previous attempts have been made to solve this problem by controlling alloying and processing to effect a bainitic phase transformation, suppressing cementite formation, and retaining carbon-enriched austenite. Most often, processing of these steels involves intercritical annealing to form a microstructure at high temperature that consists of both carbon-depleted ferrite and (somewhat) carbon enriched austenite, which is further enriched through carbon partitioning during formation of bainitic ferrite in carefully selected alloys. A limitation of this approach is the processing constraint that is needed to control the bainite transformation. The time/temperature/alloying approaches are quite challenging, especially to match with the thermal characteristics of commercial processing facilities. In the case of bainite transformations, carbon partitioning and growth of the body-centered phase are coupled.

Conventional processing of cold-rolled TRIP sheet steels to produce retained austenite that uses the bainitic transformation is typically performed in continuous annealing or hot-dip coating lines, according to the simplified thermal process schematic shown in Figure 1. Intercritical annealing is conducted to recrystallize the cold-rolled ferrite, and to create controlled amounts of ferrite and austenite in the microstructure. The austenite is cooled

from the intercritical annealing temperature (IAT) to the bainitic transformation temperature (BTT), where it decomposes to bainitic ferrite and carbon-enriched austenite. Special alloying additions, typically silicon, aluminum, or phosphorus, are made to suppress carbide formation during the bainite transformation. During final cooling, some martensite may form, but if sufficient carbon-enrichment of the austenite is achieved, then significant amounts of austenite can be retained, resulting in the desired TRIP microstructure.

SUMMARY OF THE INVENTION

The present invention recognizes that the carbon partitioning and growth of the body-centered phase are decoupled in martensite transformations and that this decoupling provides a mechanism for controlling the austenite fraction and its carbon concentration (the kinetics of carbon partitioning are separate from the mechanisms of ferrite formation), since the extent of martensite transformation is controlled primarily by temperature only, rather than both time and temperature. This new concept provides additional flexibility for implementing more convenient or less costly processing strategies or methodologies for producing steel with retained austenite.

In one embodiment of the method, a steel alloy is subjected to a heating step to produce austenite. The temperature to which the alloy is brought during the heating step is selected to achieve either full or partial austenitization. Subsequent to the heating step, the steel alloy is subjected to a quenching step that brings the alloy to a temperature within the temperature range at which martensite is produced. Subsequent to the quenching step, the alloy is subjected to a carbon partitioning step by bringing the alloy to a carbon partitioning temperature, i.e., a temperature at which there is substantial carbon mobility. Typically, there is a range of temperatures at which there is substantial carbon mobility. Within this temperature range, carbon is transferred from the martensite to the austenite to enrich the austenite so that when the alloy is cooled to the ambient application temperature, typically room temperature, the austenite is stable.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a time vs. temperature schematic of the conventional transformation induced plasticity (TRIP) steel bainite processing to produce steel with retained austenite;

Figure 2 depicts a time vs. temperature schematic of a process for producing steel with retained austenite that comprises a step of partitioning carbon to austenite; and

Figure 3 depicts the austenite volume fraction for various partition times for a sheet steel.

DESCRIPTION OF THE INVENTION

The present invention is directed to a process to produce steels with carbon-enriched retained austenite based on a new understanding of the fundamentals of carbon partitioning in martensite/austenite mixtures. It should be appreciated that the process is broadly applicable to steels that contain more than just martensite plus austenite (and indeed the TRIP steels that are used in the following example of the method contain substantial fractions of equiaxed ferrite). It should further be appreciated that although some bainitic transformation of the retained austenite could also occur in parallel with the carbon partitioning step of the present invention, such bainitic transformation processes can be controlled by alloying so as to influence bainite transformation kinetics to provide an additional variant to the microstructures achieved with the process of the present invention.

Generally, the process involves: (a) heating the steel to form austenite (either completely or partially); (b) quenching the steel to a temperature, usually above ambient, that is in the temperature range at which martensite forms (M_s to M_f , where M_s defines the upper temperature boundary of the range and M_f defines the lower temperature boundary of the range) to create controlled amounts of martensite and retained austenite; and (c) thermally treating the steel to partition carbon into the austenite, and thereby increase the chemical stability of the austenite.

From a metallurgical perspective, it should be appreciated that the present invention differs profoundly from the conventional quenching and tempering processes. Namely, conventional quenching and tempering processes are designed to temper the martensite, typically combining the available carbon in the form of carbides, and decomposing the retained austenite. Further, there is no intent to partition the carbon to austenite in these treatments. In contrast, in the present invention, formation of iron carbides is intentionally suppressed, and the austenite is intentionally stabilized rather than decomposed.

The present invention is believed to have potential application wherever carbon-enriched retained austenite offers improved product characteristics. Several applications are envisioned, including (1) high strength sheet steel; (2) high strength bar and forging steels; (3) higher carbon steels, such as carburized gears and bearings; and (4) austempered ductile

cast iron. Presently, these types of steel are particularly applicable to ground transportation vehicles.

EXAMPLE:

The present invention is described with respect to the production of retained austenite in one transformation induced plasticity (TRIP) sheet steel. TRIP sheet steels are of great current interest for automotive sheet applications and high strength products that make use of controlled amounts of retained austenite, typically on the order of 10% austenite. TRIP sheet steel with retained austenite, such as that produced by processes that use bainite transformation, typically in excess of 1% carbon (by weight) in the austenite, are capable of undergoing martensite transformation during deformation. This capability provides several advantages that are useful in various applications. For example, TRIP sheet steel with retained austenite has improved formability, and increased energy absorbance (such as would apply to a vehicle collision in automotive application).

The microstructures for the TRIP sheet steel of this example also contain equiaxed ferrite, along with different amounts of high strength constituents such as bainite and pearlite, which provide various desired properties known to those skilled in the art. It should, however, be appreciated that the present invention does not require any of these additional constituents to realize a TRIP sheet steel with carbon enriched austenite that is stable or metastable at room temperature or an application temperature. Further, to the extent that additional constituents are employed, a greater or lesser number of constituents can be employed and the relative amounts of such constituents can be varied depending on the desired microstructure. Further, the use of additional constituents to achieve desired properties is applicable to steels other than TRIP sheet steel.

The present process offers an alternative approach to conventional TRIP sheet production, and a method is explained here, to design steel alloys and processing parameters (i.e. especially the temperatures used during the present process), to achieve desired microstructures. The range of microstructures available via the present process is also greater than may be achieved via conventional bainitic processing. A schematic for the present process is shown in Figure 2, which would apply to processing of cold-rolled and coated sheet products that use an annealing process. The schematic diagram includes the annealing temperature (AT), the quench temperature (QT), and the partitioning temperature PT. For this example, an alloy of composition 0.15C is considered, typical of TRIP products where

the carbon level is limited somewhat by weldability constraints. The alloy might also contain manganese (and possibly other hardenability additions), perhaps 1%, to suppress undesired reactions during cooling, and significantly elevated silicon levels, perhaps 1.5%, to suppress carbide formation. Other elements such as N, Al, S, are also contained in typical sheet steels, but are not considered in detail for this example.

The annealing step causes recrystallization of the cold-rolled structure, and establishes the initial austenite. The annealing temperature can be above the A_3 , providing full austenitization, or in the intercritical regime between A_1 and A_3 (A_1 being the temperature at which austenite begins to form), providing both ferrite and austenite. The carbon content of the austenite is important, and is equal to the overall carbon concentration of the steel in the case of full austenitization (i.e. $C_\gamma = C_{\text{alloy}}$). For annealing in the intercritical regime, the amounts of ferrite and austenite, and their carbon concentrations, are established by the applicable phase equilibrium at the selected temperature. These values, for example, can be calculated in Fe-C binary alloys just using the phase diagram, or the appropriate tie line may be calculated in multicomponent alloys using standard thermodynamic software packages, such as ThermoCalc. Reasonable estimates can also be made using published correlations for the A_3 temperature, as shown below in Equations 1 and 2. For the example 0.15C, 1.0Mn, 1.5Si steel considered here, A_3 could be estimated using the expression of Andrews:

$$A_3(^{\circ}\text{C}) = 910 - 203\sqrt{C} - 15.2Ni + 44.7Si + 104V + 31.5Mo + 13.1W \quad (1)$$

Where C is carbon by weight percentage, Ni is nickel by weight percentage, Si is silicon by weight percentage, V is vanadium by weight percentage, Mo is molybdenum by weight percentage, and W is Tungsten by weight percentage. The calculated A_3 for this steel is about 898°C, but more importantly, at a given intercritical annealing temperature, we can modify the same expression to estimate the carbon content in the austenite via:

$$\sqrt{C_\gamma} = \frac{-AT(^{\circ}\text{C}) + 910 - 15.2Ni + 44.7Si + 104V + 31.5Mo + 13.1W}{203} \quad (2)$$

where AT is an annealing temperature in the intercritical regime and C_γ is the carbon by weight percentage in the austenite phase. At 810°C in this steel, the estimated carbon

concentration in the austenite is 0.68%. The phase fractions can be estimated using the lever rule:

$$f_a = \frac{C_\gamma - C_{alloy}}{C_\gamma - C_\alpha}, \text{ and} \quad (3)$$

$$f_\gamma = \frac{C_{alloy} - C_\alpha}{C_\gamma - C_\alpha} \quad (4)$$

where f_a is the amount of ferrite by weight percentage, C_γ is the carbon by weight percentage in the austenite phase, f_γ is the amount of austenite by weight percentage, C_α is carbon by weight percentage in the ferrite phase, and C_{alloy} is the carbon content in the steel overall, by weight percentage. The carbon content in ferrite is low, and $C_\alpha \sim 0$ can be used to give an approximate solution for the purpose of illustration in this example. At 810°C in the 0.15C, 1.0Mn, 1.5Si steel, about 78% ferrite, plus 22% austenite, are anticipated.

During the quenching step, which occurs after the annealing step, the ferrite remains essentially unchanged and the austenite transforms partially to martensite, depending on the relationship between the quenching temperature (QT), and the M_s temperature of the remaining austenite. M_s and M_f define the temperature range over which martensite forms. See Figure 2. The M_s temperature can be estimated using another correlation of Andrews:

$$M_s (^{\circ}\text{C}) = 539 - 423C - 30.4Mn - 12.1Cr - 17.7Ni - 7.5Mo \quad (5)$$

where C is carbon by weight percentage, Mn is manganese by weight percentage, Cr is chromium by weight percentage, Ni is nickel by weight percentage, and Mo is molybdenum by weight percentage. For a fully austenitized steel of this composition ($C_\gamma=0.15\%$), the M_s temperature is about 456°C, although for austenite at an intercritical annealing temperature of 810°C ($C_\gamma \sim 0.68\%$), the M_s temperature is about 355°C.

Conventional bainitic processing of these steels is normally conducted at temperatures of about 400°C or somewhat higher, and thus martensite formation is usually precluded. If quenching is carried out to a temperature below M_s , however, then controlled amounts of martensite and retained austenite can be obtained. The expression of Koistinen and Marburger, for the purpose this example, can be modified to estimate the transformed martensite fraction (f_m):

$$f_m = f_y^{AT} (1 - e^{-1.1 \times 10^{-2} (M_s - TQ)}) \quad (6)$$

where f_y^{AT} is the amount of austenite just prior to quenching, i.e. 22% in this example. For this example, if the quench temperature is 150°C, then about 12% martensite is formed during the quench, along with the remaining 10% austenite, and 78% equiaxed ferrite.

Following the quenching step, the steel is subjected to a carbon partitioning step to transfer carbon from the martensite to the austenite, thereby stabilizing the steel prior to final cooling to room temperature. The maximum amount of carbon enrichment that can be obtained during the partitioning treatment is given by the "constrained paraequilibrium" (or CPE) condition. Constrained paraequilibrium defines the endpoint of carbon partitioning in the absence of either short- or long-range diffusion of iron or substitutional atoms, which applies to martensite/austenite mixtures at low temperatures where the α/γ interface is stationary. The recently developed CPE theory indicates that the austenite in the present example could be enriched in carbon to a level of approximately 1.5% at a partitioning temperature (PT) of about 450°C, while the martensite is depleted to quite low carbon levels. (The essence of the CPE theory involves a condition where the chemical potential of carbon is equal in the α and γ phases, in the absence of substantial carbide formation, and the α/γ interface is effectively stationary, i.e. constrained, at usual partitioning temperatures.) At this level of carbon enrichment, the austenite is stable after final cooling to room temperature. The partitioning kinetics are also temperature dependent, but suitable partitioning should be able to be accomplished under time/temperature conditions that are usually employed for bainitic transformation (the required time is also dependent upon microstructural and other factors). In the present process, only carbon partitioning is required during this treatment, whereas bainitic ferrite growth in addition to carbon partitioning is required for conventional bainitic processing. Thus, for this example, the steel composition and processing parameters used here produce a final microstructure of 78% equiaxed ferrite, 12% carbon-depleted martensite, and 10% retained austenite (having approximately 1.5% carbon). Such a microstructure is expected to represent a commercially viable TRIP product. Using the present process, other microstructure variants can be designed by altering the steel composition and critical processing parameters. Some of these microstructures would be difficult to achieve by conventional processing, and the new process allows the potential for

higher levels of carbon enrichment in the austenite, increasing strength via formation of lath martensite in the microstructure, and application to Si/Al-containing iron castings.

Example results are shown in Figure 3, obtained for a 0.19C, 1.46Mn, 1.96 Al sheet steel., intercritically annealed for 180 s at 805°C to create a ferrite/austenite starting microstructure, followed by quenching to 284°C, and then partitioning for various times and temperatures (between 300 and 450°C) shown in the figure. The final austenite fraction after complete processing is shown. This example shows that substantial quantities of retained austenite are achieved by Q&P processing, where the quenching temperature was carefully selected to control the transformed microstructure prior to quenching.

What is claimed is:

1. A method for producing a steel alloy with retained austenite comprising the acts of:

providing a steel alloy;

annealing, following said step of providing, said steel alloy at an annealing temperature to produce austenite in said steel alloy;

quenching, following said step of annealing, said steel alloy at a temperature to transform at least a portion of said austenite into martensite;

carbon partitioning, following said step of annealing, said steel alloy to transfer carbon from said martensite to said austenite; and

cooling, following said step of carbon partitioning, said steel alloy to a desired temperature.

2. A method, as claimed in claim 1, wherein:

said step of providing comprising providing a low-carbon steel alloy.

3. A method, as claimed in claim 1, wherein:

said step of annealing comprising placing said steel alloy at a temperature greater than a temperature for full austenization.

4. A method, as claimed in claim 1, wherein:

said step of annealing comprising placing said steel alloy at an intercritical temperature that is at or above the temperature at which austenite begins to form and below the temperature for full austenization.

5. A method, as claimed in claim 1, wherein:

said step of quenching comprising placing said steel alloy at a temperature below the temperature at which martensite starts to form.

6. A method, as claimed in claim 1, wherein:

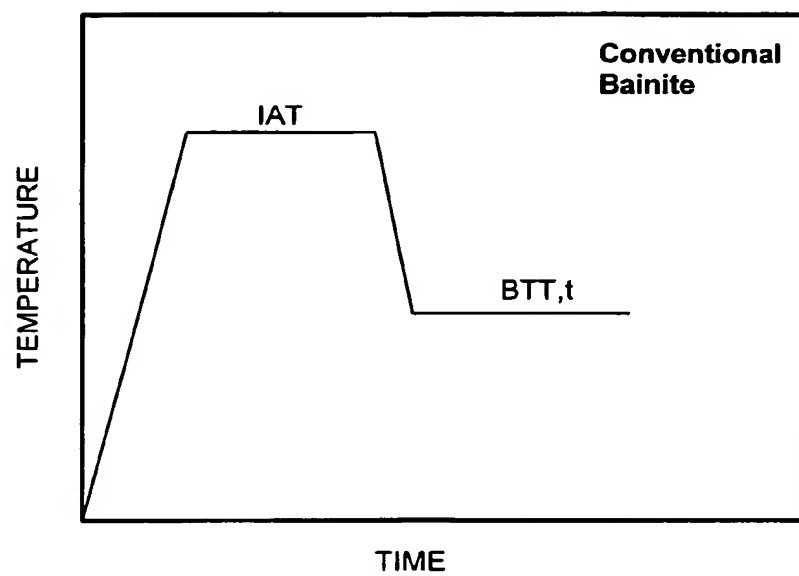
said step of quenching comprising placing said steel alloy at a temperature at which martensite forms.

7. A method, as claimed in claim 1, wherein:
said step of carbon partitioning comprising placing said steel alloy at a temperature at which there is carbon mobility.

8. A method, as claimed in claim 1, wherein:
said step of carbon partitioning comprising placing said steel alloy at a temperature above which martensite starts to form.

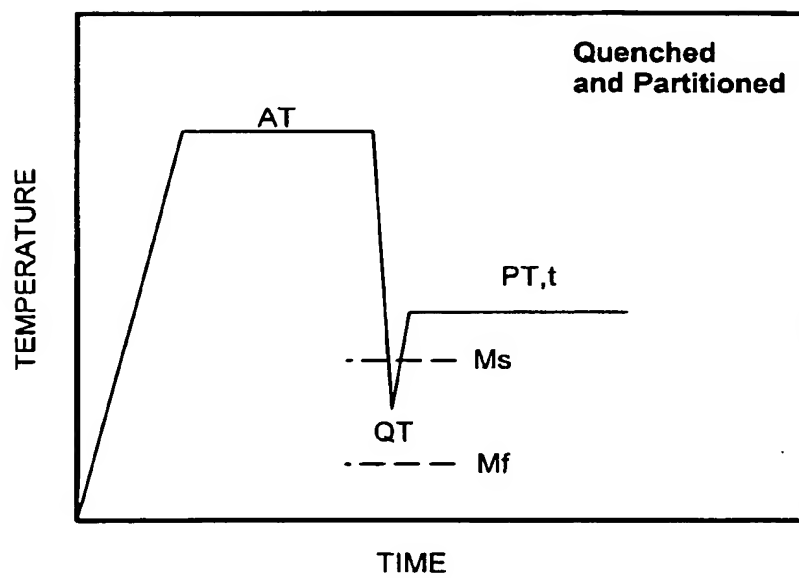
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FIG.1



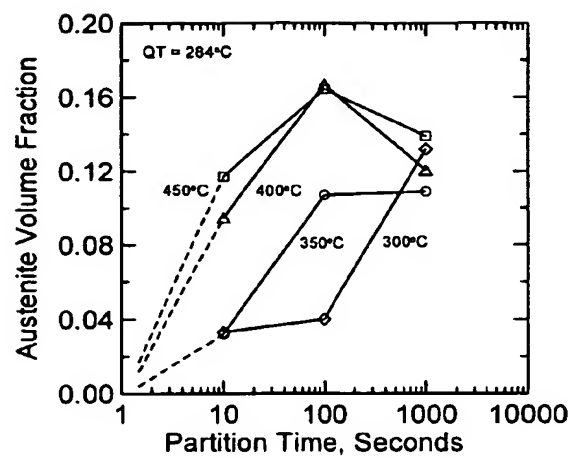
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FIG.2



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FIG.3



INTERNATIONAL SEARCH REPORT

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: austenitic, martensitic, cooling or quenching

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,544,422 A (RAO) 01 October 1985	1-8

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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